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## (54) BLEACHING COMPOSITIONS


(71) We, COLGATE-PALMOLIVE COMPANY, a corporation organized and existing under the laws of the State of Delaware, United States of America, of 300 Park Avenue, New York, New York 10022, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—


The invention here presented is broadly in the field of bleaching; more particularly it relates to activators for oxygen-releasing compounds and relates especially to activators formed from peracid precursors.

The use of per-compounds which liberate hydrogen peroxide such as inorganic perhydrates, which, when dissolved liberate hydrogen peroxide enclosed in their crystal lattice (e.g. perborates, perphosphates, persilicates) and peroxides which yield hydrogen peroxide by hydrolysis (e.g. sodium peroxide or certain percarbonates) in domestic or industrial laundering is well known. There are, in particular, detergent compositions in which per-compounds such as sodium perborate frequently comprise between 1% and 35% of the total composition.

Hydrogen peroxide and the precursors which liberate it in solution are good oxidizing agents for removing certain stains from cloth, especially stains caused by wine, tea, coffee, cocoa, fruits, etc. However, hydrogen peroxide and its precursors have been found to bleach quickly and most effectively only at a relatively high temperature, e.g. about 80°C to 100°C. Since it is often impracticable or inconvenient to boil the wash water the full potential of oxygen bleaches has not yet been realized because of their poor bleaching at temperatures below 80°C. Since these bleaches are relatively safe both in concentrated form and on colours, and since they can be formulated directly in the detergent, it is desirable to provide a process for bleaching with per-oxygen compounds and compositions containing them, which provide effective bleaching and stain removing properties at temperatures below boiling, e.g. 25°—80°C.

Most bleaching is done in an alkaline mediium. It is believed, without being limited to any theory, that hydrogen peroxide ionizes in an alkaline medium into a hydrogen ion and a negatively charged perhydroxyl ion. The perhydroxyl ion can react with additional hydrogen peroxide to yield active oxygen which is also negatively charged. Both the perhydroxyl ion and the active oxygen ion can bleach by oxidizing a substrate by electron transfer. Since materials to be bleached are usually negatively charged, the material and the perhydroxyl ion or active oxygen mutually repel each other and it takes high temperatures before the perhydroxyl ion or active oxygen has sufficient energy to overcome this repulsion. An activator which has a higher oxidation potential than the per-compound alone would result in improved bleaching at lower temperatures.

It is known that peracids which are formed from hydrogen peroxide and an acid are stronger oxidizing agents than hydrogen peroxide itself. However, peracids are relatively unstable and cannot be used as such but only formed *in situ* from a peroxygen compound such as sodium perborate and a suitable peracid precursor.

The present invention relates to a process and composition for forming peracids *in situ* in order to obtain significant bleaching effects at temperatures below boiling, e.g. 25°—80°C, preferably 50°—70°C.

According to one aspect of the invention, in a process for bleaching materials a fabric or other textile material to be bleached is contacted with an aqueous washing solution containing an effective amount of an oxygen-releasing per-compound, an alkyl ester or an acetal, and an ester-hydrolyzing enzyme.

According to another aspect of the invention a bleaching composition comprises an oxygen-releasing per-compound, an alkyl ester or an acetal, and an ester-hydrolyzing enzyme.

The alkyl ester or the acetal and the ester-

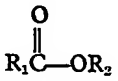

[Price 33p]

hydrolyzing enzyme are precursors in the formation of peracids *in situ*, i.e., in bleaching solution. The reactive carboxylic group formed reacts with the per-compounds to form peracids which have the requisite bleaching effects at temperatures below boiling, e.g. 25°—80°C.

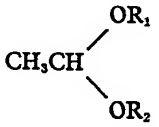
Per-compounds which are oxygen-releasing and employable in the present invention may be hydrogen peroxide, alkali metal peroxides such as sodium perborate and potassium perborate, alkali metal perphosphates such as sodium perphosphate and potassium perphosphate, alkali metal persilicates, such as sodium persilicate and potassium persilicate, and alkali metal percarbonates such as sodium percarbonate and potassium percarbonate.

The per-compounds are generally present in the ratio by weight of per-compound to ester in the range of 1:6 to 6:1, the preferred ratios being 0.5:3 to 2:1. The per-compounds are typically present in bleaching compositions in amount of from 1 to 40% by weight, preferably 3 to 20% and more, preferably 5 to 15%, by weight of the total composition.

The alkyl esters employable in the present invention may have the general formula:



wherein $R_1$ is the residue of an alaphatic monocarboxylic acid and has 1 to 10, e.g. 1 to 8, carbon atoms and $R_2$ is the alkyl moiety of the ester and has 1 to 10, e.g. 1 to 8 carbon atoms in its chain. Examples of preferred alkyl esters are alkyl esters of acetic acid such as methyl acetate, ethyl acetate, propyl acetate, isopropyl acetate and other alkyl esters of aliphatic acids such as methyl-butyrate, ethyl butyrate, propyl butyrate and isopropyl butyrate. Acetals having the formula



wherein $R_1$ and $R_2$ are radicals having 2 to 8 carbon atoms in their chain may also be used.

The amount by weight of ester or acetal employable in the bleaching process and composition is dependent upon the amount of per-compound present.

The ester-hydrolyzing enzymes are usually specific for the simple aliphatic esters preferably employed in this invention. Generally, the ester-hydrolyzing enzymes this invention makes use of are esterases and lipases. Examples of preferred esterases are acetylesterase and carboxylesterase. These esterases hydrolyze carboxylic esters and have wide distribution in mammalian tissues, insects, plants, citrus fruits and fungi. A preferred preparation is from horse liver [Connors, W. M., Pihl, A., Dounce, A. L. & Stotz, E. (1950), J. Biol. Chem. 184, 29; Burch, 1954], with a specific activity of 0.25 m-mole of ethyl butyrate/mg. protein N/min.

Examples of preferred lipases are plant lipases, pancreatic lipase and gastric lipase. These lipases also hydrolyze carboxylic esters and are present in mammalian pancreas and oats. A preferred preparation is from pig pancreas [Sard, L. Marchis-Mouren, G., Constantin, M. J. & Desnuell, P. (1957), Biochim, Biophys. Acta, 23, 264], with a specific activity of 63 m-moles of olive oil/mg. protein N/min.

The amount of enzyme employed depends upon the amount of ester or acetal present. The weight ratio of ester or acetal to enzyme is generally in the range of 30:1 to 5:1, preferably 20:1 to 10:1. The amounts of enzyme required also vary with the specific activity of the enzyme employed. With regard to the recited ratio, it is assumed that the specific activity of the enzyme employed is of the order of magnitude set out above.

The bleaching process may be carried out in the presence of, and the bleaching compositions may contain, organic detergent selected from soap, synthetic organic detergents and mixtures thereof.

Examples of suitable water-soluble soaps include the water-soluble salts, e.g. the sodium, ammonium, and alkylolammonium salts of higher fatty acids or resin acids containing 8 to 20 carbon atoms, preferably 10 to 18 carbon atoms. Suitable fatty acids can be obtained from oils and waxes of animal or vegetable origin, e.g. tallow, grease, coconut oil, tall oil and mixtures thereof. Particularly useful are the sodium and potassium salts of the fatty acid mixtures derived from coconut oil and tallow, e.g. sodium coconut soap and potassium tallow soap.

Synthetic organic detergents employable in the present invention may be anionic, nonionic, amphoteric, polar nonionic or cationic detergents.

Examples of suitable anionic detergents include water-soluble sulphated and sulphonated synthetic detergents having an alkyl radical of 8 to 26, preferably 12 to 22 carbon atoms, in their molecular structure.

The usual nonionic surfactants can be used, such as condensation products of alkyl phenols or alkylthiophenols with ethylene oxide or other ethylene oxide condensation products with higher fatty alcohols and monoesters of hexahydric alcohols.

The amphoteric detergents which can be used are generally water-soluble salts of deri-

vatives of aliphatic amines which contain at least one cationic group, e.g. non-quaternary nitrogen, quaternary ammonium, or quaternary phosphonium group, at least one alkyl group of 8 to 18 carbon atoms and an anionic water-solubilizing carboxyl, sulpho, sulphato, phosphate or phosphono group in their molecular structure. The alkyl group may be straight chain or branched and the specific cationic atom may be part of a heterocyclic ring.

The polar nonionic detergents include open-chain aliphatic amine oxides of the general formula

$$R_1R_2R_3N \rightarrow O,$$

$R_1$ being an alkyl, alkenyl, or monohydroxyalkyl radical having 10 to 16 carbon atoms and $R_2$ and $R_3$ each being methyl, ethyl, propyl, hydroxyethyl or hydroxypropyl radicals.

The usual cationic detergents can be used such as the diamines of the general formula

$$RNHC_2H_4NH_2,$$

wherein R is an alkyl group of 12 to 22 carbon atoms, or compounds having the general formula

$$R'CONHC_2H_4NH_2$$

wherein R' is an alkyl group of 12 to 18 carbon atoms, or quaternary ammonium compounds.

Anionic or nonionic surfactants are preferred, particularly higher alkyl benzene sulphonates, higher alkyl sulphates and higher fatty acid monoglyceride sulphate.

The concentration of the water-soluble soaps and synthetic organic detergents in the compositions will generally be in the range of from 4 to 40%, preferably 15 to 35%, by weight.

The compositions can also contain conventional ingredients such as builder salts. Suitable representatives include the following: trisodium phosphate, tetrasodium pyrophosphate, sodium acid pyrophosphate, sodium tripolyphosphate, sodium monobasic phosphate, sodium dibasic phosphate, sodium hexamethaphosphate, sodium metasilicate, sodium silicate ($Na_2O/SiO_2$ of 1/1.6 to 1/3.2), sodium carbonate, sodium sulphate, borax, ethylene diamine tetraacetic acid tetrasodium salt, trisodium nitrilotriacetate, citrates, e.g. sodium citrate, citric acid, glycollates, e.g. sodium glycollate, phosphonates, diphosphonates, organic polyelectrolytes, e.g. vinyl methyl ether-maleic anhydride interpolymers and water-soluble salts thereof (e.g. alkali metal, ammonium or amine); polymaleic anhydride and water-soluble salts (e.g. sodium, potassium or ammonium) and mixtures thereof.

Usually substantial amounts of compatible builder materials will be present in compositions, the amounts being in order of 40 to 90% by weight, preferably 65 to 85% by weight of the composition. The compositions may also contain other conventional ingredients, for example, antiredeposition agents such as sodium carboxymethyl cellulose; suds builders such as ammonia, amides, N-alkyl amides and alkanolamides of fatty acids (e.g. the monoethanolamide of coconut oil fatty acids, and lauroyl and myristoyl glycerol amides, ethanol amides and isopropanol amides); optical bleaching agents; colour; and perfume.

The following Examples illustrate this invention:

EXAMPLE I

| | Percent by Weight |
|---|---|
| Sodium linear tridecyl benzene sulphonate | 35.0 |
| Anhydrous pentasodium tripolyphosphate | 40.0 |
| Sodium perborate | 8.0 |
| Ethyl butyrate | 8.0 |
| Acetylesterase | 0.8 |
| Perfume | 0.5 |
| Moisture and additives such as brighteners and colour | 7.7 |
| | 100.0 |

EXAMPLE II

| | Percent by Weight |
|---|---|
| Sodium tetrapropylbenzene sulphonate | 12.0 |
| Sodium carbonate | 35.0 |
| Potassium persilicate | 30.0 |
| Propyl acetate | 10.0 |
| Carboxylesterase | 0.5 |
| Perfume | 0.5 |
| Moisture and additives such as brighteners and colour | 2.0 |
| | 100.0 |

EXAMPLE III

| | Percent by Weight |
|---|---|
| Sodium dodecylbenzene sulphonate | 18.0 |
| Sodium tripolyphosphate | 35.0 |
| Monoethanolamide of coconut oil fatty acid | 2.5 |
| Sodium silicate | 7.0 |
| Sodium sulphate | 9.0 |
| Magnesium silicate | 1.0 |
| Sodium perborate | 5.0 |
| Ethyl acetate | 10.0 |
| Pancreatic lipase | 0.5 |
| Perfume | 1.0 |
| Moisture and additives such as brighteners and colour | 11.0 |
| | 100.0 |

A washing solution is prepared by dissolving 12.5 grams or 5 grams per litre of any of the compositions recited in Examples I—III in tap water having a hardness of 50 ppm. Soiled household laundry is immersed in the washing solution for 10 minutes at about 50°C and stirred, after which the laundry is removed, rinsed in water and dried. The bleaching effects are observed. Broadly, the improved process for bleaching comprises contacting the fabric or textile material to be bleached with an aqueous washing solution containing effective amounts of an oxygen-releasing per-compound, an alkyl ester or acetal and an ester-hydrolyzing enzyme, e.g. at temperatures in the range from 25°C to 80°C for from 1 up to 30 minutes, preferably at about 50°C for 5 to 15 minutes. The material to be treated may be pre-soaked or allowed to stand in the aqueous washing solution or the solution containing the material may be stirred or agitated.

WHAT WE CLAIM IS:—

1. A process for bleaching materials in which a fabric or other textile material to be bleached is contacted with an aqueous washing solution containing an effective amount of an oxygen-releasing per-compound, an alkyl ester or an acetal, and an ester-hydrolyzing enzyme.

2. A process according to Claim 1 in which the weight ratio of the per-compound to the ester or acetal is in the range from 1:6 to 6:1 and the weight ratio of the ester or acetal to the enzyme is in the range 30:1 to 5:1.

3. A process according to Claim 1 or Claim 2 in which the aqueous solution also contains a detergent selected from soap, synthetic organic detergents and mixtures thereof.

4. A process according to any of the preceding Claims wherein the per-compound is selected from hydrogen peroxide, alkali metal peroxides, perborates, perphosphates, persilicates and percarbonates.

5. A process according to any of the preceding Claims in which alkyl ester has the general formula

$$R_1C(=O)—OR_2$$

wherein $R_1$ and $R_2$ have 1 to 10 carbon atoms each.

6. A process according to any of the preceding Claims in which the enzyme is selected from esterases and lipases.

7. A process according to any of the preceding Claims which is performed at a temperature in the range 25°C to 80°C.

8. A bleaching process according to Claim 1 and substantially as herein described.

9. A bleaching composition comprising an oxygen-releasing per-compound, an alkyl ester or an acetal and an ester-hydrolyzing enzyme.

10. A bleaching composition according to Claim 9 wherein the per-compound is selected from hydrogen peroxide, alkali metal peroxides, perborates, perphosphates, persilicates and percarbonates.

11. A bleaching composition according to Claim 9 or Claim 10 in which the alkyl ester has the general formula

$$R_1C(=O)—OR_2$$

wherein $R_1$ and $R_2$ have 1 to 10 carbon atoms each.

12. A bleaching composition according to any of Claims 9 to 11 wherein the ester-hydrolyzing enzyme is selected from esterases and lipases.

13. A bleaching composition according to Claim 12 wherein the esterase is selected from acetylesterase and carboxylesterase and the lipase is selected from plant lipases, pancreatic lipase and gastric lipase.

14. A bleaching composition according to any of Claims 9 to 13 wherein the weight ratio of the per-compound to the ester or acetal is in the range from 1:6 to 6:1 and the weight ratio of the ester or acetal to the enzyme is in the range 30:1 to 5:1.

15. A bleaching composition according to any of Claims 9 to 14 wherein the per-compound is present in an amount of from 1% to 40% by weight of the total composition.

16. A bleaching composition according to any of Claims 9 to 15 containing an organic detergent selected from soap, organic synthetic detergents and mixtures thereof.

17. A bleaching composition according to Claim 16 wherein the organic detergent is present in an amount of from 4% to 40% by weight of the total composition.

18. A bleaching composition substantially as described in any of the Examples.

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